Office of Technical Assistance Research Proposal

Metal Surface Finishing with Plasma

Background

More than 20 companies are engaged in the production of machined stainless steel components from various grades of steel in the state. Most of these companies have to undertake a cleaning step and a passivation step before products are packaged for their customers. The passivation of steel products consumes a lot of nitric acid. TURA filers in metal processing, for the years 1994 to 1998, reported an average annual usage of about 2.0 million pounds of nitric acid. The actual amount used for passivation is included in this total usage. In addition, various toxic chemicals such as hydrochloric acid, sodium dichromate, etc. are used in the cleaning processes preceding the passivation step. A lot of fresh water is used for final rinsing and a lot of energy in the form of dry hot air is used in the final steps of the operation.

Passivation is a complex process by which clean stainless steel surface is given a thin film of oxide layer coating that makes the surface chemically passive and highly corrosion resistant. Traditionally, passivation is carried out with wet chemicals. Although it is claimed that the use of chemicals is not actually necessary, since the protective film will form spontaneously in an oxygen rich environment, provided that the surface has been thoroughly descaled and cleaned. The rate of autopassivation is unpredictable.

The wet chemical process uses toxic chemicals - nitric acid, sodium dichromate - to passivate. From investigation, this appears to be the standard practice in the US. The companies engaged in passivation consider the process stages and the compositions of their baths proprietary. From literature, it is known that typical baths contain 20 to 60% nitric acid (67% by weight) by volume and about 4-oz./gal sodium dichromate. Immersion time varies from 10 to 60 minutes and operating temperature varies from room temperature to 160^{o}F. Depending on the type of steel, the concentrations of the chemicals may vary and additional chemical treatment steps may be required. For example, for 400 Series ferritic or martensitic steel parts, it is required that the parts be additionally immersed in an aqueous solution containing 4 to 6 weight % of sodium dichromate at 140 to 160^{o}F for 30 minutes. Thorough rinsing with clean water and forced-air drying would then follow this immersion.

Majority of the small companies contracts out the passivation of their products. This mode of operation does not allow the companies maximum control of their production and delivery schedules.

Scope of Problem

At very low pressure, (vacuum conditions) and under excitation by radio frequency, a gas plasma consisting of a large concentration of highly excited atomic, molecular, ionic and radical species can be generated from many non-polluting gases. This radio frequency activated gas plasma has been developed into a process of surface treatment that has numerous applications including effective cleaning and removal of organic contaminants from metal surfaces. The generated high energy particles bombard the surface, break the chemical bonds of the contaminant to produce smaller components which boil off (ablate) and are removed by the vacuum. Other systems have employed gas plasma for reactive ion etching, enhanced chemical vapor deposition and polymerization to deposit thin layers on substrates. There have been commercial applications of this process to various surfaces but the process has never been developed and used to passivate stainless steel.

Objectives

The gas plasma technology for passivation of stainless steel will be designed to use nitrogen/oxygen or any non-polluting gas as the plasma gas. The assumption is made that after washing and cleaning to remove gross contaminants such as grease, oil, iron filings, dust and other particulate matter, the remaining surface contaminants will be thin films of carbohydrates and or hydrocarbons. The carbohydrates and/or hydrocarbons will react with the energized oxygen particles to produce water and carbon dioxide which will be swept from the plasma chamber by the vacuum pump, that is maintaining the vacuum in the chamber. Nitriding of the surface iron atoms with the nitrogen as well as selective formation of chromium oxide by reaction with oxygen will render the surface passivated. A quick literature survey has shown that the chemically passive and corrosion resistant layer on stainless steel contains these compounds.

One company that OTA has worked with will like to employ a process or technology, in-house, which is economical and environmentally friendly. The company has successfully passivated coupons of 455 stainless steel in a laboratory scale plasma chamber using nitrogen as the plasma gas. One of the company's clients performed some basic tests for chemical passivity and corrosion resistance on its stainless steel medical/surgical products. The results were found to be comparable or superior to similar products conventionally passivated.

Scope of Work

There is still a lot of basic information about the process to be developed before the process can be commercialized. Fundamental investigation should be conducted to look into the following areas:

- Establish the chemical composition, the physical structure and thickness of the corrosion resistant layer.
- Identify the chemical, the various species formed in the plasma and the variation in the composition of the reactive species formed at different operating conditions.
- Develop a plausible reaction kinetic model to enable the prediction of surface properties including the thickness of the corrosion resistant layer.
- Investigate plasma generation from more complex chemical compounds.
- Use plasma to generate substrate surface finishes of specified and defined deposit or layers of deposits for example as a substitute for coatings and paintings.
- Compare properties of such plasma generated finishes with conventional surface finishes.